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**Plutonium(VI) and (V) reactions with Fe(III)OOH: A sorption and XAFS study.**

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The volume of nuclear wastes from weapons and power production in the United States currently exceeds 600 million cubic meters. The constituents of this waste include actinides (Th, U, Np, Pu, Am, Cm), the lighter fission products (mainly Tc, Cs, Sr) and a host of other inorganic and organic materials from nuclear fuel processing. For remediation and risk assessment purposes, the processes by which the actinides interact with the environment must be known.

The complexity of environmental systems requires that tractable model systems be studied so that the effects of competing processes such as redox, complexation with inorganic and organic matter, surface precipitation and complexation can be assessed. Understanding these subsystems at the molecular level is necessary for understanding the driving forces of the larger, more complex environmental system.

The interaction of plutonium with goethite, a well characterized, and common iron oxy-hydroxide has been studied. Previous studies with this system have shown that Pu(IV) and Pu(V) adsorb to goethite, and that the surface of goethite may be responsible for the reduction of Pu(V) to Pu(IV)[1,2]. Experiments with Pu(VI) show that it adsorbs to goethite, and that the presence of goethite causes a reduction of Pu(VI) to Pu(IV) as shown by XANES and UV-Vis spectra. The role of the disproportionation of Pu(V) in these systems is under study. Understanding these phenomena and the role of the goethite is hindered by the complexity of the chemistry of Pu under environmental conditions.

Experiments with Pu(VI) and goethite in the presence of carbonate show that in the pH region where $Pu(VI)(CO_3)_3^{4-}$ is predicted to form, pH ≈ 9 and above, adsorption of Pu to the surface of the goethite is inhibited. The mechanism for this process could be explained by electrostatic terms whereby the negatively charged surface of goethite (pH > 8.9) creates a repulsion between the negatively charged Pu complex. This is important for understanding the migration of the Pu through the environment.

Experiments to study the structure of the adsorbed Pu species have been performed. Using synchrotron based XANES (x-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure), the identity of the oxidation state of the adsorbed plutonium ion, the bond lengths, and coordination numbers of the ligands bound to the plutonium ($OH^-$, $CO_3^{2-}$, etc.) can be studied. Experiments have shown inner-sphere complexation of plutonium(IV) with the surface of goethite in the case of Pu(V) and Pu(VI).

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